Aluminous-Ferruginous Oxide Mineral Nodules in Tropical Soils[1]

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ABSTRACT: Secondary oxide mineral nodules occur in the ferruginous, ferruginous bauxitic, and bauxitic soils of the Hawaiian Islands. The concentration of these oxide nodule aggregates which are larger than 2 mm ranges from 5 per cent in some ferruginous soils to as high as 85 per cent in the ferruginous bauxitic soils of the Halii family. The nodules are formed by the process of induration in which the hydrated amorphous hydroxide and oxides are dehydrated to their crystalline oxide form. The resulting indurated oxide nodule becomes an independent unit in the soil system with corresponding loss of effective surface even though the nodule may contain friable clay material in its interior. The typical nodule produced in the ferruginous bauxitic soil has a dense iron oxide layer (hematite and maghemite) and, in the interior, soft to hard, lighter-colored material which contains gibbsite.

MANY OF THE tropical latosols of the Hawaiian Islands have a high content of secondary mineral oxide nodules occurring in the surface and near-surface horizons of their soil profiles. Sherman et al. (1967), reported the occurrence of these oxide nodules in the Halii soils, a ferruginous bauxitic latosol (typic gibbsihumox), and described the morphology of the nodules and their chemical composition. The description of the soil profile located the greatest concentration of the nodules in the surface horizon. The physical analyses of this horizon showed that the surface horizon contains as high as 85 per cent mineral oxide nodules greater than 2 mm in diameter. The nodules ranged in size from 2 to 50 mm with some being as large as 100 mm. The nodules of the Halii soils have an irregular, roughly oval shape and a polished surface. When the nodule is broken, the cross section reveals a jet black, dense outer layer ranging from 0.5 to 1 mm in thickness surrounding a much lighter-colored, soft, friable, and sometimes powdery silty clay material in the interior, as shown in Figure 1. The boundary between the dark hard black outer layer and the lighter-colored interior material is sharp and distinct, giving the effect of a coating as contrasting as that shown in the diagrammatic drawing of the nodule (Fig. 1).

The occurrence of the hard mineral oxide nodules is not limited to the ferruginous bauxitic latosols of the Hawaiian soils. A similar high concentration of ferruginous nodules is found in the surface horizon of soil belonging to the Kunuweia series of the Humic Ferruginous Latosol Group (Plinthic Acrorthox) on the island of Molokai. Likewise, soils of the Naiwa series (Oxic Dystrandepts) of the same great soil group occurring along the Waimea Canyon on Kauai have a high concentration of ferruginous nodules. These nodules were described by Sherman and Kanehiro (1954) as ferruginous concretions. Gibbsitic nodules have been described by Sherman and Matsusaka (1965) occurring in the Koolau soils (Aeric Tropaquepts). Bates (1959) and Sherman (1957) described the formation and separation of gibbsitic mineral aggregates when hydrated mixed amorphous oxides of aluminum, iron, and silicon were dehydrated in the Akaka soils of the Hydrol Humic Latosol Group (Typic Hydrandepts).

In the past, these nodular oxide materials have been described as concretions, lateritic gravels, ironstone, and ferruginous coated fragments of lava (Cline et al., 1955). These nodules are not concretions, since there is no evidence in their physical features to suggest their

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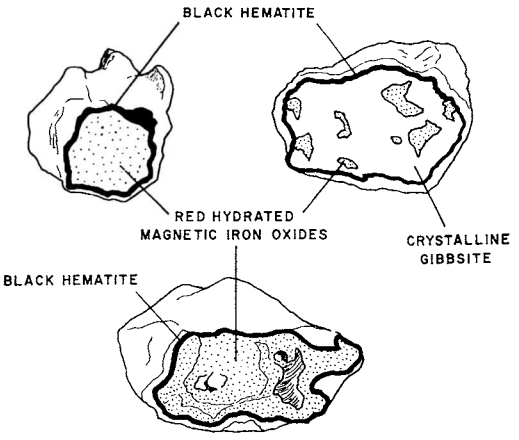

FIG. 1. Ferruginous aluminous nodules showing the relative positions of the oxides after crystallization.

development by accretion as defined by Todd (1903) for concretions. The polished, rounded outer surface is similar to that of many concretions. However, the rather dense outer layer and the soft interiors indicate a different mode of development.

The term "nodule" was introduced by Bryan (1952) of Australia to describe these nodular aggregates in order to distinguish them from concretions. Soil nodules, according to Bryan, are the product of pedogenetic processes. Taylor and Pohlen (1962) stated that nodular bodies are formed in soils by three processes: (1) by accretionary deposition around a nucleus with the progressive enlargement of the nodule which will form concretions, plates, tubular concretions, and rhizoconcretions; (2) by ingrowth or diffusion of surface material to form enriched residual aggregates; and (3) by irreversible induration without either outgrowth or ingrowth of the surface of the aggregate. These authors pointed out the importance of soil nodules of all types in the statement, "Soil nodules provide evidence not only of current soil conditions but also of past processes." In addition they stated, "Nodule formation is more evident in mature soils owing to the greater degree of weathering." They emphasized also the relationship between advanced stages of weathering and nodule formation: "Nodulated aggregates, which are mostly ferruginous, are a feature of the senile tropical and subtropical soils which have colloids that become irreversibly aggregated on dehydration."

The oxide nodules of the Hawaiian soils must be the product of the advanced stages of pedogenetic weathering for the following reasons:

(1) The nodules occur in surface or near-surface horizons of the soil profile, and these horizons are parallel to the topographic surface and bear no relationship to the underlying geologic strata.

(2) Field observations indicate that these nodular aggregates develop progressively from their irreversible induration by dehydration from hydrated oxide clays as the product of intense weathering and leaching conditions.

The object of this study is to elucidate the mode of origin of these oxide nodules. The study will identify the conditions for nodule formation and the physical, chemical, and mineralogical changes occurring during their development.

METHOD OF INVESTIGATION

Field Observations and Collections

A large number of soil profiles has been examined over the past years in the Hawaiian Islands. These observations were supplemented by many field observations in Queensland, Australia; on the laterite soils of the Southern Province of Sudan; the bauxitic soils of New Zealand; and the buried concretionary laterites of the region along the Blue Nile at Sennar, Sudan. Large numbers of nodules were collected for this study from re-examined profiles of the bauxitic soils of the Hawaiian Islands with special emphasis on their mode of origin.

Laboratory Studies

The samples were brought into the laboratory where each nodule was separated into two fractions. The first fraction was material from the hard, dark-colored surface layer, and the second represented the soft, lighter-colored material of the interior. The hardness of the surface material of the ferruginous bauxitic nodules occurring in the Halii soil facilitated the separation. In samples in which the iron oxide was low in parent clayey bauxitic saprolite, it was impossible to make the separation due to the thinness of the hard outer layer. The separated

samples were chemically analyzed for their oxide content by methods described by Jackson (1958). The oxides were identified by X-ray defraction methods supplemented by differential thermal analysis. The latter method is essential in describing the relationship between amorphous hydrated hydroxide and oxides, and the same constituents in their crystalline form, as proposed by Sherman (1962) and Sherman et al. (1964). This relationship is based on the observations reported by Bates (1959) and Sherman (1957) on the differential crystallization of gibbsite from colloidal gel containing Al-Fe-Si. Dias (1964) has shown that soils of the Hydrol Humic Latosols, which have a very high concentration of amorphous hydrated hydroxides and oxides, will crystallize to oxides when they lose 40 to 50 per cent of their water. The crystallized oxide does not regain its amorphous oxide state by rewetting. This system conforms to the hydroxide-oxide system proposed by Tamura and Jackson (1953).

Thin sections were prepared of several of the nodules. Observations on these sections were limited to the lighter material of the interior of the nodule.

EXPERIMENTAL RESULTS AND OBSERVATIONS

The field observations provide some evidence as to the origin of the mineral oxide nodules. These nodules occur only in the surface horizon, and in a virgin profile they become less numerous with depth. They occur to the depth of the surface dehydration and in the zone which is subject to frequent wetting and drying. The soil aggregates become decreasingly indurated with depth, those near the surface having the characteristics described in Figure 1. In soils having a surface disturbed by plowing for several years the entire surface horizon to the depth of the disturbed area becomes indurated and eventually nodules form similar to those shown in Figure 1. A freshly exposed surface soft-soil aggregate will indurate in as little as 24 hours, but the development of the hard surface coating will take 5 to 10 years of wetting and drying. Field observations do not support the hypothesis that the hard surface layers are due to precipitation of iron oxide on the surface, for the following reasons: (1) the rapid drainage of rain water which prevents sufficiently prolonged contact for solution of iron and its deposition; (2) the change in color of the interior of the indurated soil aggregate; and (3) the development of a porous structure in the interior and an increasing thickness of the hard coating.

As the hard surface coating develops, the nodule becomes progressively more impervious. Eventually neither roots nor water can penetrate the mineral nodule and thus it then contributes the properties of a gravel fraction to the soil. The soil as a whole loses specific surface in the process, with the result that it becomes inert to the chemical reaction processes of the soil and its solutions—a condition referred to as the senile stage by Taylor and Pohlen (1962).

Another type of mineral nodule formation results in rather pure gibbsitic nodules formed by the movement of gels of aluminum hydroxide into voids in the soil or its exudation from surfaces of ditch banks where it is crystallized to gibbsite by dehydration. Figure 2 is a photograph of a bulbous aggregate of oxide nodules formed on a ditch bank by this process.

The data presented in Table 1 were obtained from the chemical analysis of mineral nodules taken from the surface horizon of three profiles of ferruginous bauxite soils of the Halii series, located on the slopes of Kilohana Crater on the island of Kauai and described by Sherman et al. (1967). These analyses show the difference in chemical composition between the mineral nodules and the soil particles less than 2 mm in size. The aluminum oxide content is very high (57 per cent) in nodules of Profile 1. On mineral analyses these nodules are shown to contain approximately 85 per cent gibbsite. The nodules from Profiles 2 and 3 have a very high content of iron oxide (62.7 and 69.7 per cent, respectively), and a much lower aluminum oxide content (14.2 and 9.2 per cent, respectively). Profiles 2 and 3 are located at a higher elevation on the slope of the crater than is Profile 1. The iron oxide content in the soil fraction of all profiles is very high (46.9, 51.1, and 61.8 per cent, respectively). The silica content of all nodules is 1.1 per cent or lower.

The data presented in Table 2 show the difference in chemical composition of the hard outer shell and the friable material of the in-

FIG. 2. The sheaf-like bulbous aggregates formed by the exudation of hydrous gels of hydroxides and oxides of aluminum which form these aggregates on dehydration and crystallization to gibbsite. (From the surface of a ditch bank on the slopes of Kilohana Crater, Kauai.)

terior of mineral aggregate collected in the Pooku area on Kauai. The iron oxide content of the outer shell is higher in all nodules, the difference ranging from 5.5 to more than 12 per cent. The aluminum oxide content was higher in the interior material, with differences ranging from 1.2 to 11.5 per cent. The silica content was very low in all parts of the nodule.

The mineral composition of the outer and inner portions of nodules reported in Table 2,

TABLE 1

CHEMICAL COMPOSITION OF THE NODULE AND SOIL FRACTIONS OF 3 PROFILES OF THE HALII SOILS (FERRUGINOUS BAUXITIC SOIL) LOCATED ON THE SLOPES OF KILOHANA CRATER, ISLAND OF KAUAI

	PROFILE 1		PROFILE 2		PROFILE 3	
	NODULE	SOIL	NODULE	SOIL	NODULE	SOIL
Depth in inches	0–5	0–5	0–3	0–3	3–8	3–8
Per cent of whole	23.9	76.1	68.5	30.7	85.1	14.9
Per cent oxide						
SiO_2	1.1	1.5	1.0	4.2	0.5	3.0
Al_2O_3	57.0	26.4	14.2	17.6	9.2	11.8
Fe_2O_3	14.0	46.9	62.7	51.1	69.7	61.8
FeO	0.5	1.5	1.9	4.1	0.8	2.1
TiO_2	1.6	6.0	3.7	4.5	3.1	4.2
MnO	0.07	0.10	0.06	0.07	0.03	0.04
CaO	0.02	0.05	0.04	0.05	0.12	0.10
MgO	0.10	0.60	0.02	0.08	0.06	0.06
K_2O	0.01	0.10	0.04	0.07	0.03	0.04
Na_2O	0.26	0.12	0.71	0.56	0.47	0.34

as determined by X-ray diffraction analysis, is given in Table 3. In general the concentration of iron oxide minerals is greater in the outer shell than in the interior. In a number of samples the gibbsite content is lower in the interior portion of the nodules than in the outer shell. This reflects the degree of crystal development rather than the true aluminum oxide con-

TABLE 2

CHEMICAL COMPOSITION OF NODULAR MINERAL AGGREGATES FROM SURFACE SOILS FROM POOKU AREA, ISLAND OF KAUAI, HAWAIIAN ISLANDS

TYPE OF NODULAR MINERAL FRAGMENT	PART OF NODULE	OXIDE ANALYSIS (PER CENT)			
		SiO_2	Al_2O_3	Fe_2O_3	TiO_2
1. Ferruginous bauxitic; dark red with hard and darker outer shell	Shell	0.41	30.01	47.13	4.23
	Interior	0.86	31.25	41.79	5.55
2. Ferruginous, with black outer shell	Shell	0.72	23.51	52.09	4.74
	Interior	3.69	28.45	42.87	4.44
3. Ferruginous bauxitic; black outer shell with yellowish-brown interior	Shell	0.61	29.57	44.82	3.19
	Interior	0.44	41.05	32.12	2.14
4. Ferruginous bauxitic; dark brown outer shell with yellowish-white interior	Shell	1.37	32.49	39.67	3.63
	Interior	2.91	43.44	27.06	2.42
5. Bauxitic; shell too fragile to save	—	—	—	—	—
	Interior	4.40	50.06	25.07	4.13
6. Flat ferruginous; purplish-black shell with grayish-black interior	Shell	0.52	13.42	67.73	7.18
	Interior	0.91	19.55	60.41	6.14

TABLE 3

MINERALOGICAL COMPOSITION OF NODULAR MINERAL AGGREGATES FROM SURFACE SOILS FROM POOKU AREA, ISLAND OF KAUAI, HAWAIIAN ISLANDS

TYPE OF NODULAR MINERAL FRAGMENT	PART OF NODULE	MINERAL IDENTIFICATION*					MAGNETITE† ATTRACTION Mgm/gm
		GIBBSITE	GOETHITE	HEMATITE	MAGHEMITE	MAGNETITE	
1. Ferruginous bauxitic; dark red with hard and darker outer shell	Shell	M	M	L	M	—	3.6
	Interior	L	L	L	L	—	2.3
2. Ferruginous, with black outer shell	Shell	M	M	L	L	—	2.6
	Interior	M	L	L	L	—	3.9
3. Ferruginous bauxitic; black outer shell with yellowish-brown interior	Shell	L	L	L	VL	—	2.3
	Interior	M	L	VL	M	—	1.5
4. Ferruginous bauxitic; dark brown surface with yellowish-white interior	Shell	H	M	—	VL	—	1.8
	Interior	M	L	—	—	L	1.1
5. Bauxitic; shell too fragile to save	—	—	—	—	—	—	—
	Interior	H	VL	—	—	L	1.9
6. Flat ferruginous; purplish-black shell with grayish-black interior	Shell	VL	M	M	M	—	1.4
	Interior	L	M	L	L	—	1.6

* X-ray diffraction: H, high; M, medium; L, low; VL, very low.
† Magnetite = 100.

TABLE 4

CHEMICAL COMPOSITION OF A NODULE IN ADVANCED STAGE OF DEVELOPMENT; MIGRATION OF IRON OXIDE HAS LEFT VOIDS IN THE INTERIOR (COLLECTED FROM A HALII SOIL ON KAUAI BRANCH EXPERIMENT STATION, KAUAI)

PORTION OF NODULE	OXIDE ANALYSIS (PER CENT)					
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	H_2O+	H_2O-
Outer shell	0.88	19.27	53.51	2.79	20.90	2.86
Inner portion	0.26	34.39	35.1	3.68	23.82	2.24

centration. The dehydration will be more intense in the outer shell than in the interior. Thin sections of these nodules do show a greater concentration of gibbsite and amorphous aluminous oxide in the interior portion of the nodule. Differential thermal analysis shows a greater oxide content in the interior due to the presence of both subcrystalline and crystalline forms of gibbsite.

In Table 4 is given the chemical composition of a secondary mineral aggregate in which the separation of aluminum and iron oxide has proceeded to a point where the material in the interior has become a very pale brown-white in color. The interior of the aggregate has become partially hollow due to movement of iron oxide in a mobile form to the surface of the nodule. The data show a definitely higher iron oxide content in the outer shell than in the interior (53.5 and 35.1 per cent, respectively), and a higher concentration of aluminum oxide in the interior than in the outer shell (34.4 and 19.3 per cent, respectively). Optical mineralogical examination of thin sections gave evidence supporting the hypothesis that the two oxides are separated by differential crystallization of gibbsite from the mixed oxide colloidal system and the migration of iron to the outer shell.

Table 5 shows the chemical composition of several gibbsitic nodules found in a Koolau clay soil on the island of Kauai. The aluminum oxide content of all nodules is high, ranging from 54.6 to 64.0 per cent. The surfaces of two of the nodules contained some kaolin clay, resulting in a higher content of silica (11.2 and 12.8 per cent, respectively). The iron oxide content of all nodules was very low probably due to complete separation of the aluminum oxide from the iron oxide which was found in layers at a greater depth below the surface of the soil.

DISCUSSION AND SUMMARY

The results of this study show that the secondary mineral aggregates commonly occurring in tropical soils, such as lateritic gravel, nodular iron oxides, ferruginous and ferruginous gibbsitic nodules, and gibbsitic nodules have developed from the crystallization of oxide minerals from the amorphous hydrated colloidal oxide fraction of strongly weathered tropical soils. Although they often resemble concretion by their physical appearance, their mode of origin is not that of concretionary deposition. Their formation is due to repeated dehydrations of the amorphous hydrated oxide gels causing a series of atomic arrangements leading to the development, first, of a subcrystalline state and, finally, a well-structured crystalline state. Growth of the mineral aggregate is enhanced by polymerization due to condensation leading to the development of stable inert aggregate units.

It is suggested that the observed order of development from a weak aggregate of mixed colloidal hydrous oxides stepwise to nodules of separated crystalline oxides has been the result of the proposed system shown in Table 6.

The mineralogical changes can be followed by several procedures. The amorphous fraction is relatively inactive to X-ray diffraction and, on differential thermal analysis, shows only the loss

TABLE 5

CHEMICAL COMPOSITION OF GIBBSITIC NODULES FROM KOOLAU SOILS ON ISLAND OF KAUAI

SAMPLE NUMBER	OXIDE ANALYSIS (PER CENT)				
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	H_2O
1	0.8	62.5	1.3	1.1	34.5
2	0.7	64.0	1.2	1.2	33.2
3	12.8	55.0	3.2	1.1	29.1
4	11.2	54.6	4.7	0.8	28.3

TABLE 6

PROGRESSIVE PHYSICAL, CHEMICAL, AND MINERALOGICAL CHANGES OCCURRING IN DEVELOPMENT OF MINERAL OXIDE NODULE FROM CLAY AGGREGATE BY INDURATION DUE TO DEHYDRATION

MINERALOGICAL FORMS

Mixed hydrous oxide gels —H_2O→ Amorphous hydrous hydroxides and oxides —H_2O→ Subcrystalline hydrous hydroxides and oxides —H_2O→ Crystalline oxide

CHEMICAL COMPOSITION

$Al(OH)_3$-$Fe(OH)_3$ →

- $Al(OH)_3$ → $Al(OH)_3$ →
  - $Al(OH)_3$ — Gibbsite
  - AlOOH — Boehmite
- $Fe(OH)_3$ →
  - FeOOH → γFe_2O_3 — Maghemite
  - $Fe(OH)_3$ →
    - $HFeO_2$ — Goethite
    - Fe_2O_3 — Hematite

PHYSICAL CHARACTERISTICS

Soft smeary clay aggregate → Clay aggregate → Firm aggregate stable to wetting → Mineral nodule

of water. The cryptocrystalline or subcrystalline oxide fraction will give thermal reaction but no reaction or only a weak reaction to X-ray analysis. Crystalline oxides have definite X-ray patterns and varied but definite thermal characteristics. The studies of Sherman (1962) have indicated that aluminum oxide has, at most, a very weak, transitory subcrystalline system and thus will separate first from the mixed colloidal hydrated oxide system, while iron oxides, having a much slower transformation system, will have stable subcrystalline forms. Thus the iron oxides are capable of shifting to a hydrated system on rewetting. This would make it possible for the iron oxide to move from the interior to the outer shell of the nodule.

The theory of progressive crystallization of the oxides is also supported by the presence of the gamma iron oxide, maghemite. Maghemite, a magnetic iron oxide, has been shown to develop from the dehydration of colloidal hydrated iron oxides (Matsusaka and Sherman, 1961). The outer shell of the ferruginous and ferruginous bauxitic nodules are magnetic and the intermediate oxide system is not.

The results of a study of the origin of secondary mineral nodules have shown that they have formed by the stepwise conversion of hydrous colloidal mixed oxide gels to separately crystallized aluminum and iron oxides. The substantiation of this hypothesis is based on the properties of the hydrous colloidal gel, the crystalline oxide system, and the intermediate minerals. The chemical, physical, and mineralogical changes can be traced from colloidal gel to the crystalline oxide nodule. The differential crystallization properties produce a separation in the nodule with the iron oxide concentrating in the outer shell and the crystalline aluminum oxide (gibbsite) remaining in the interior of the nodule.

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